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THE BAND SYSTEMS OF ALKALI VAPORS

W. Weizel and M. Kulp

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16. Abstract

A number of band edges of the molecules, Na_2, K_2, NaK, NaCs, LiK, LiRb, LiCs and NaRb are arranged in edge schemes. The vibrational quanta of the base terms and the upper terms can be approximately determined. Viewpoints are produced for interpreting electron terms. The terms of Na_2 are interpreted as terms of a photo-electron.

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The band systems of alkali vapors*

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Up to now, of the absorption spectra of alkali vapors, only a few band systems in red and green have been studied. Through the studies of Wurm[1] we are familiar with a red and a green band system of Li_2. Two similar band systems of Na_2 have been analyzed by Loomis and Wood[2], Fredrickson and Watson[3], and Fredrickson[4]. A red[3] and an ultra-red[5] system are known for K_2. The band systems of these three metals are entirely analogous; in each case the one of greater wavelength is a $\Sigma \rightarrow \Sigma$ transition and the one of a shorter wavelength is a $\Sigma \rightarrow \Pi$ transition. The lower term is in all cases the base term of the molecule, i.e. a straight $^1\Sigma$ term. The interpretation of these band systems can be greatly simplified as follows:

Li_2 rot [1]	$A \longleftrightarrow B$	$3p\sigma\,^1\Sigma \longleftrightarrow 2s\sigma\,^1\Sigma$	← Absorpt
Li_2 grün [2]	$A \longleftrightarrow C$	$2p\pi\,^1\Pi \longleftrightarrow 2s\sigma\,^1\Sigma$	→ Emissio
Na_2 rot	$A \longleftrightarrow B$	$4\pi\sigma\,^1\Sigma \longleftrightarrow 3s\sigma\,^1\Sigma$	
Na_2 grün [2]	$A \longleftrightarrow C$	$3p\pi\,^1\Pi \longleftrightarrow 3s\sigma\,^1\Sigma$	
K_2 ultrarot [3]	$A \longleftrightarrow B$	$5p\sigma\,^1\Sigma \longleftrightarrow 4s\sigma\,^1\Sigma$	
K_2 rot [1]	$A \longleftrightarrow C$	$4p\pi\,^1\Pi \longleftrightarrow 4s\sigma\,^1\Sigma$	

Key: 1 red; 2 green; 3 ultra-red.

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* By W. Weizel and M. Kulp. Report from the Physical Institute of the University of Rostock.

With 2 Figures. Submitted Feb. 27, 1930.

** Numbers in margin indicate foreign pagination.

As a convenient designation, we have introduced the abbreviations $A \leftrightarrow B$ and $A \leftrightarrow C$ for the band systems.
In addition to these bands, a band system in orange has also been analyzed by Ritschl and Villars[6]. We have also used the designation $A \leftrightarrow$ for this system, as we believe that there will still be another band system in red for NaK.
J.M. Walter and S. Barratt[7] are still studying a large number of band edges of the molecules Na_2, K_2, Rb_2, Cs_2, LiK, LiRb, LiCs, NaK, and NaRb, mainly in the shorter wavelength areas. Walter and Barratt have not attempted an classification of these bands.
We set ourselves the task of evaluating the data of Walter and Barratt, even though these data are not very precise. The authors do not make any assertions as to the accuracy of their measurements and they give their values only in whole Angstrom units. Thus it can be assumed that there may be measurement errors up to 0.5 Å. This means that combined differences can produce errors up to 1 Å, and in particularly unfavorable cases even greater errors will have to be assumed. Expressed in cm this corresponds at 4500 Å to a permissible deviation of 5 cm^{-1}, and at 3500 Å to about 8 cm^{-1}.
Naturally, this lack of exactness means that the combination ratios lose some of their proving power and in many cases they make several different arrangements possible. On the other hand, sometimes the intensity data can be used to verify the classification. The arrangement of the bands is also supported to a certain extent by analogies with the bands that have already been classified in red and green.
By and large, the edge schemes given in the following can be consi- /973
dered corrrect. In any case, the vibrational quanta of both the upper and lower states have been measured correctly. However, it is possible that in a few cases the enumeration of the vibrational states should be raised by one or two units.

Na_2

Walter and Barratt give a long list of band edges for Na_2 in ultraviolet; these we have been able to arrange, with very few exceptions, in five band systems. In the following edge schemes v' means the

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Na_2. System $A \leftrightarrow B$

v'/v''	0	1	2	3	4
0			29 824	29 941	30 058
			(117)	(117)	
			(159)	(161)	(171)
1		29 551	29 665	29 780	29 887
		(114)	(115)	(107)	
		(148)			
2	29 283	29 403			
	(120)				
	(154)				
3	29 129				
	(152)				
4	28 977				
	(150)				
5	28 827				
	(149)				
6	28 678				
	(155)				
7	28 523				

v'/v''	0	1	2	3	4
0			2	3	3
1		8	6	6	1
2	8	8			
3	10				
4	10				
5	8				
6	4				
7	1				

vibrational quantum number of the upper term and v" the number for the lower term. We have given in parentheses the differences between bands that are next to or above one another; these are also the vibrational quanta. The intensities are given in a small diagram that is similar to the main diagram in design. /974

The vibrational quanta of the lower term A in the system $A \leftrightarrow B$ is found to be 158 cm^{-1} and for the upper term B' it is 115 cm^{-1}. The pure electron frequency of the band system v_0 (the base line) is: v_0 = 29,590 cm^{-1}.

The system $A \leftrightarrow C'$ could not be observed for v" > 1, as the bands are covered by the series line of sodium at [redacted] = 3303 Å. The average value for the vibrational quantum of the lower term A is 151 cm^{-1}; for the vibrational quantum of the upper term C' one obtains about 103 cm^{-1}, v_0 = 30,432. The vibrational quantum of the lower term A in the system $A \leftrightarrow D$ is 156 cm^{-1}; for the lower term D it is 95 cm^{-1}, v_0 = 31,329 cm^{-1}. /975

Na_2. System $A \leftrightarrow C'$

v'' \ v'	1	2	3	4	5	6	7
0	30 535	30 638	30 741	30 836	30 941	31 037	
		(103)	(103)	(95)	(105)	(96)	
		(159)	(150)	(144)	(152)	(153)	
1		30 479	30 591	30 694	30 789	30 884	30 979
			(112)	(103)	(95)	(95)	(95)

v'' \ v'	1	2	3	4	5	6	7
0	2	4	4	1	1	1	
1		4	4	4	2	1	1

Na_2. System $A \leftrightarrow D$

v'' \ v'	0	1	2	3	4
0	31 329	31 428			
	(99)				
	(156)	(158)			
1	31 173	31 270	31 359		
	(97)	(89)			
	(155)	(155)	(157)		
2	31 018	31 115	31 202	31 500	31 388
	(97)	(89)	(98)	(88)	
				(156)	(147)
3				31 141	31 241
				(97)	

v'' \ v'	0	1	2
0	2	1	
1	2	2	1
2	1	1	2
3			

Na_2. System $A \leftrightarrow B''$

v'' \ v'	0	1	2	3
0			33 683	33 797
			(114)	
			(158)	(159)
1		33 413	33 525	33 638
		(112)	(113)	
		(156)		
2		33 257		
		(154)		
3	32 983	33 103		
	(120)			
	(152)			
4	32 831			
	(150)			
5	32 681			
	(149)			
6	32 532			

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Na_2-System $A \leftrightarrow C''$

v'' \ v'	0	1	2	3	4	5	6
0	33 900	34 004	34 108	34 213	34 319	34 413	34 52[illegible]
		(103)	(104)	(105)	(106)	(94)	(107)
	(160)	(161)					
1	33 740	33 843					
		(103)					

The lower term A of the system $A \leftrightarrow B''$ has the vibrational quantum 156 cm^{-1}; the upper term B" has a vibrational quantum of 117. The $v'' \rightarrow v' = 0 \rightarrow 3$ and $v'' \rightarrow v' = 1 \rightarrow 3$ bands can also be classified equally well in the the system $A \leftrightarrow C''$ [shown on page 4]. v_0 = 33,450. /975

The vibrational quantum for the lower term A is 160 in the system A $\leftrightarrow$ C"; the vibrational quantum for the lower term C" is 106. v_0 = 33,900. /976

Interpretation of the Na_2 bands

The intensity distribution makes it possible to see immediately the obvious analogy between systems $A \leftrightarrow C'$ and A $\leftrightarrow$ C" and between systems A $\leftrightarrow$ B' and A $\leftrightarrow$ B". The vibrational quantum of the lower term is about equal for all the band systems, as should also be the case for absorption bands. In this we see a strong support for the accuracy of the classification. Of course, the vibrational quantum for the lower term A should also be the same as the vibrational quanta for the red green Na_2 bands. This is in fact the case. Fredrickson and Watson give 157-158 cm^{-1} for the vibrational quantum of the base term for Na_2.

The bands arranged here can be interprested very simply as higher serial members of the red and green Na_2 bands. The systems A $\rightarrow$ B' and A $\rightarrow$ B" should belong to the system A $\rightarrow$ B (red bands) and the ssytems $A \rightarrow$ C' and A $\rightarrow$ C" should belong to the system A $\rightarrow$ C (green bands). The terms C, C' and C" form approximately a Rydberg series. In order to calculate the terms it is more expedient to represent them by means of the Ritzsche term formula, since there are clear deviations from the Rydberg formula. One can then calculate the fol-

lowing term values: C'' = 5270, C' = 8740, C' = 18870. From the combination A $\leftrightarrow$ C' one obtains the term value for the base term, and using this one can then obtain the B terms and the D term.

The following table gives the term values for the Na_2 terms and the relevant effective quantum numbers. The third column then gives the interpretation of the term and the 4th. column gives the vibrational quantum. The 5th. column shows the presumed state of the Na atoms in which the term dissociates. /977

	Termwert	n_{eff}		ν_e	
A	39 170	1,67	$3s\sigma\,^1\Sigma$	157	$3s\,^1S + 3s\,^1S$
B	24 160	2,13	$4p\sigma\,^1\Sigma$	116	$3s\,^1S + 3p\,^1P$
B'	10 580	3,22	$5p\sigma\,^1\Sigma$	115	$3s\,^1S + 4p\,^1P$
B''	5 720	4,37	$6p\sigma\,^1\Sigma$	117	$3s\,^1S + 5p\,^1P$
C	18 870	2,41	$3p\pi\,^1\Pi$	124	$3s\,^1S + 3p\,^1P$
C'	8 740	3,54	$4p\pi\,^1\Pi$	103	$3s\,^1S + 4p\,^1P$
C''	5 270	4,57	$5p\pi\,^1\Pi$	106	$3s\,^1S + 5p\,^1P$
D	7 840	3,74	$4f\sigma, n\,^1\Sigma\,\Pi$	95	$3s\,^1S +$?

Termwert = term value

The effective quantum numbers in this table are extremely interesting. They demonstrate the great decrease in the $p\sigma$-electrons pertaining to p and s, which can already be seen in the case of hydrogen - H_2 and continues with He_2. This lowering in value can already be seen in the case of the $p\pi$-electrons. Unfortunately, the gap between He_2 and Na_2 is so great that this phenomenon cannot be studied with the degree of accuracy one would like. In particularly, one cannot determine whether the main quantum numbers for the $p\sigma$-electrons should be raised by one.

K_2

We have been able to put some of the lines that Walter and Barratt give for K_2 into the following edge scheme A $\leftrightarrow$ D.
We already mentioned above an ultra-red and a red band system for K_2 and we explained their electron terms. The intensity distribution of this new system in blue is not unlike that for red. Also, the

/978

K_2-System $A \leftrightarrow D$

v'' \ v'	0	1	2	3	4	5	6	7
0			23 083	23 142	23 206	23 266	23 320	23 380
			(59)	(64)	(60)	(54)	(60)	
			(90)	(91)	(91)			
1	22 872	22 929	22 993	23 051	23 115			
	(57)	(64)	(58)	(64)				
	(94)	(89)	(90)					
2	22 778	22 840	22 903					
	(62)	(63)						
	(88)							
3	22 690							
	(97)							
4	22 593							

$\nu_0 = 22\,936\ cm^{-1}$

v'' \ v'	0	1	2	3	4	5	6	
0			1	6	8	7	5	
1	0	3	5	2	0			
2	1	4	1					
3	3							
4	2							

vibrational quantum for the base term agrees with that of the red system and is 91; the vibrational quantum for the upper term is about 60. Since shorter wave band systems are not observed for K_2, an interpretation of the electron term cannot be attempted, however. /977

NaK /978

We have arranged some of the band edges in the range 4014 to '353 Å given by Walter and Barratt in the following edge scheme A ⟷ D. The classification of the bands in this system is not entirely clear. For this reason, we have listed the two band edges 26,089 and 25,967 in two places. The vibrational quantum for the upper term is about 82, while for the lower term it is about 120 cm^{-1}. The latter value agrees with the base vibrational quantum of the red NaK system. It is not possible to attempt an interpretation of the electron term for these bands.

From the other band edges given by Walter and Barratt even more edge sequences can be determined that belong to one or several systems. Since, however, this classification is uncertain and ambiguous, we will just mention here that between 24,906 cm^{-1} and 25,438 cm^{-1} 9 edges can be classified in a system with the vibrational quanta 120 cm^{-1} and 83 cm^{-1}, and between 27,747 cm^{-1} and 28,257 cm^{-1}

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/979

NaK System A ⟶ D

0	1	2	3	4	5	6	7	8	9
26 089	26 164	26 253	26 329	26 413	26 490	26 574	26 652	26 738	26 816
	(75)	(89)	(76)	(94)	(77)	(84)	(78)	(86)	(78)
(122)	(123)	(123)	(117)	(118)		(119)	(120)	(121)	
25 967	26 041	26 130	26 212	26 295		26 455	26 532	26 617	
	(74)	(82)	(82)	(83)		(77)	(85)		
(121)	(115)	(123)	(123)						
25 846	25 926	26 007	26 089						
	(80)	(81)	(82)						
(120)	(120)	(114)	(122)						
25 726	25 806	25 893	25 967						
	(80)	(87)	(74)						
(125)	(120)	(127)							
25 601	25 686	25 766							
	(85)	(80)							
(117)		(126)							
25 484		25 640							
(110)									
25 374									

v' \ v''	0	1	2	3	4	5	6	7	8	9
0	1	2	1	1	1	1	1	0	0	1
1	2	1	2	1	1		2	2	1	
2	1	4	2	1						
3	10	8	2	2						
4	10	4	2							
5	8		4							
6	4									

10 edges can be classified in a system with the vibrational quanta 128 and 63 cm^{-1}. In addition to these systems, another system is known in orange, which has been classified by Ritzschl and Villers[8]. We have called this system, in order to distinguish it from the one examined in this study, A ⟷ C.

NaCs

/980

For NaCs Walter and Barratt found bands in yellow-green and purple. All the edges in yellow-green we placed in system A ⟷ D, except for the three with the shortest wavelengths, which, if one is to judge by their intensity, certainly belong to a second system.

The striking absence of the 3 ⟶ 1 and 4 ⟶ 1 bands in this system /981 is probably the result of the fact that these edges were not noticed as they were overshadowed by the very strong bands 18,039 and 17,940.

NaCs. System A ⟶ D

v'' \ v'	0	1	2	3	4	5
0	18 233	18 300	18 364	18 428	18 493	18 555
		(67)	(64)	(64)	(65)	(62)
	(96)	(97)	(98)			
1	18 137	18 203	18 266			
		(66)	(63)			
	(98)	(95)				
2	18 039	18 108				
		(69)				
	(94)					
3	17 945					
	(99)					
4	17 846		17 974			
	(92)		(93)			
5	17 754	17 820	17 881			
	(66)	(61)				
	(101)					
6		17 719				
	(93)					
7		17 626				
	(93)					
8		17 533				
	(92)					
9		17 441	17 508			
		(67)				

v'' \ v'	0	1	2	3	4	5
0	3	10	10	10	2	0
1	7	10	3			
2	10	5				
3	10					
4	10		3			
5	10	1	3			
6		7				
7		5				
8		1				
9		1	1			

NaCs. System A ⟶ E

v'' \ v'	0	1	2	3	4	5	6	7
0	23 951	24 014	24 078	24 236	24 395	24 461	24 618	24 666
	(63)	(64)	(65)	(59)	(66)	(102)	(55)	(48)
	(91)	(97)	(93)	(100)	(114)	(54)		
1	23 860	23 917	24 171	24 336	24 509	24 563		
	(102)	(97)	(64)	(66)	(54)			
	(90)	(97)	(93)	(99)				
2	23 758	23 820	24 270	24 371				
	(101)	(62)	(58)	(101)				
	(90)		(105)					
3	23 668		24 107					
	(101)		(93)					
4	23 567		24 014					
			(63)					
			(91)					
5			23 860					
			(102)					
			23 758					
			(90)					
6			23 668					
			(101)					
7			23 567					

v'' \ v'	0	1	2	3	4	5	6	7
0				2	4	6	4	2
1		4	4	6	6	6		
2	6	6	10	6	6			
3	6	6	6	6				
4	6	6	10					
5	6	6						
6	4							
7	2							

The base state and the activated state have the vibrational quanta 96 cm^{-1} and 65 cm^{-1}.

The purple NaCs bands obviously belong to several systems. The most definite and strongest of these these we have listed above as A ⟷ E.

The band edge 0 ⟶ 3 is probably covered by the strong band 24,461. /982 The vibrational quantum 87 cm^{-1} agrees with that of the yellow-green system. The upper term has the vibrational quantum 62. A second system can still be set up. Since, however, it can be arranged in several ways, it is not listed here. It consists of 14 bands between 4034 and 3931 Å. Its vibrational quanta are 99 and 47 cm^{-1}. We did not interpret the upper electron term in any of the NaCs systems.

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Walter and Barratt also give a few band edges for the lithium compounds of the heavier alkali metals and for sodium rubidium. It is scarcely possible to avoid arranging the few edges arbitrarily. Therefore, we are giving the edges themselves once again. We have mainly attempted a classification because we found it tempting to /982 /983 to try to find regularities in the vibrational quanta. Even if some changes have to be made in the classification, this does not alter the amount of the vibrational quanta.

The vibrational quanta for the base terms are 207 cm^{-1} for LiK, 185 cm^{-1} for LiRb, 167 cm^{-1} for LiCs, and 100 cm^{-1} for NaRb. For the upper term they are 126 cm^{-1} for LiK, 81 cm^{-1} for LiRb, 77 cm^{-1} for LiCs, and 62 cm^{-1} for NaRb.

Comparison of the vibrational quanta of the various molecules

Figures 1 and 2 show the vibrational quanta of some of the terms of the molecules Li_2, LiK, LiRb, LiCs (Fig. 1) and Na_2, NaK, NaRb, and NaCs (Fig. 2). The upper curves, designated by A, represent the vibrational quanta of the base terms and the lower curves the vibrational quanta of the activated states, designated C*). Since the states of the various molecules designated by C are perhaps not all comparable, the C curves are somewhat problematic.

However, if one also takes into account that for the higher Na_2 terms vibrational quanta have been found that are always approximately equal, about 100-110, then the upper terms of the other molecules will also not differ very much. To this extent one can also assign a certain significance to the C curves. The A curves demonstrate clearly the regular connection between the base vibrational quanta /984 of the various molecules. The vibrational quanta decrease with the heaviness of the molecule, however the decrease is most substantial for the lighter molecules, especially between Li_2 and Na_2. Out of two molecules with a very similar molecular weight, e.g. Na_2 and

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*) The values for Li_2, Na_2 and NaK are taken from the studies of K. Wurm, F.W. Loomis and R.W. WOod, and R. Ritzschl and D. Villars.

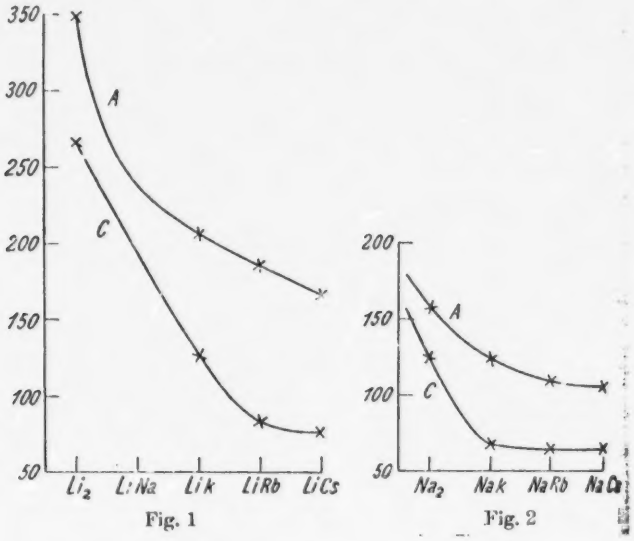

Fig. 1 Fig. 2

Vibrational quanta of the C and A terms

LiK, both having molecular weights of 46, the one consisting of various components demonstrates the higher vibrational quantum in the base state.

The vibrational quanta of the upper terms appear to approach rapidly a maximum limit that lies at about 60-70 cm^{-1} when one increases the molecular weight. It makes no difference how this increase occurs. Evern higher terms would probably show even better this advance towards a maximum value for heavy molecules.

Unfortunately, it is not possible to discuss these interesting relationships in more detail, as there is insufficient observation material.

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